

- 1 -

**DESCRIPTION****LAMINATED METALLIC SHEET FOR CAN****TECHNICAL FIELD**

The present invention relates to a laminated metallic sheet for can, used for metallic can and can lid by working thereof after heat treatment such as baking finish and baking print.

**BACKGROUND ART**

In recent years, the can manufacturing industry studies the application of laminated metallic sheet fabricated by laminating a thermoplastic resin film on a metallic sheet. Particularly from the points of corrosion resistance, safety, and heat resistance, there have been given the proposals relating to the laminated metallic sheet for can using polyester resin as the laminate because the polyester resin represented by polyethylene terephthalate has well-balanced characteristics.

The term "laminate" designates, in a wide sense, making plywood, or plating resin films, aluminum foils, papers, and the like together. The term referred to herein designates coating at least one side of metallic sheet by a resin film.

For example, JP-B-60-47103, (the term "JP-B" referred to herein signifies the "Examined Japanese Patent Publication"), provides a laminating method for polyester film, where a polyester resin is fused onto a metallic sheet at or above the melting point of the resin. The patent publication discloses a technology to

form an amorphous polyester layer in the vicinity of interface with the metallic sheet, which amorphous layer then improves the adhesion between the metallic sheet and the film.

JP-A-10-138389 and JP-A-10-138390, (the term "JP-A" referred to herein signifies the "Unexamined Japanese Patent Publication"), disclose a technology to improve the adhesion between a metallic sheet and a film after working, by adjusting the amorphous polyester layer in the vicinity of interface with the metallic sheet to a low orientation state giving 0.010 or smaller double refraction index, and specifying the percentage of the thickness of the amorphous layer to the total thickness of the film to a range from 40 to 90%.

The laminated metallic sheets described in above three patent publications show excellent workability when as-laminated metallic sheet is formed to can body and can lid, (hereinafter also referred to as the "can manufacturing work"). If, however, the can manufacturing work is given after painting or printing on the laminated metallic sheet in order to give decorative appearance, indication of contents, indication of cautions, and the like, cracks are generated in the film during the can manufacturing work stage because the film on the metallic sheet is deteriorated by the heat of baking step for the paint and print.

Considering the above problems, the present invention has an object to provide a laminated metallic sheet for can, which laminated metallic sheet has excellent workability giving no crack in the resin film on the metallic sheet even when the can manufacturing work is applied after heat treatment such as baking

finish and baking print.

#### DISCLOSURE OF THE INVENTION

The present invention provides a laminated metallic sheet for can, which laminated metallic sheet has a polyester resin film containing about 50% by mole or more of polyethylene terephthalate on at least one side of a metallic sheet, and shows about 22 to about 25  $\text{cm}^{-1}$  of half value width of shift peak caused by the C=O stretching vibration at  $1730 \pm 20 \text{ cm}^{-1}$  in the Raman spectra, using a linear polarization laser light, on the film of the laminated metallic sheet for can after heat treatment. The heat treatment for the laminated metallic sheet for can is preferably at least one treatment selected from the group consisting of baking finish and baking print.

For the laminated metallic sheets for can, the polyester resin is preferably a copolyester containing about 50% by mole or more of ethylene terephthalate component. The copolyester is more preferably a copolyester obtained from terephthalic acid, isophthalic acid, and ethylene glycol.

Furthermore, the present invention provides a laminated metallic sheet for can having excellent post-heat-treatment workability, which laminated metallic sheet has a polyester-based resin containing polyethylene terephthalate as the main component, being laminated on a metallic sheet, and showing 22 to 25  $\text{cm}^{-1}$  of half value width of Raman shift peak caused by the C=O stretching vibration in the vicinity of  $1730 \pm 20 \text{ cm}^{-1}$  in the Laser Raman spectrometry using a linear polarization laser light on the film

surface layer of the laminated metallic sheet for can after heat treatment.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 shows the relation between the shift position of the C=O stretching vibration and the spectral intensity in Raman spectra of various kinds of polyethylene terephthalates having different densities with each other.

Figure 2 shows the relation between the density of polyethylene terephthalate and its half value width of the peak of C=O stretching vibration in Raman spectra.

Figure 3 shows the observed values in relation to the Raman spectral observation point on a resin layer cross section and the half value width of the peak of C=O stretching vibration for laminated metallic sheets generated cracks in the film after heat treatment.

Figure 4 shows the observed values in relation to the Raman spectral observation point on a resin layer cross section and the half value width of the peak of C=O stretching vibration for laminated metallic sheets which did not generate cracks in the film after heat treatment.

Figure 5 shows an example of the laminating facility of thermofusion type.

Figure 6 shows the relation between the half value width of the peak of C=O stretching vibration in Raman spectra and the leak current on the surface layer of film.

#### **BEST MODE FOR CARRYING OUT THE INVENTION**

The present invention is described in detail in the following.

The inventors of the present invention conducted detail studies on the film for laminating metallic sheet, which film does not generate cracks during the can manufacturing work stage and can lid working stage even after the heat treatment such as baking finish and baking paint, and have found that, for a metallic sheet laminated with a polyester film containing polyethylene terephthalate, (hereinafter referred to also as PET), as the main component, precise control of the degree of crystallinity of amorphous crystals (spherulite) formed in the film layer after the heat treatment is effective.

The term "heat treatment" referred to herein designates the heating of a work to, normally, temperatures approximately ranging from 150°C to 220°C for several minutes to several tens of minutes before can manufacturing and can lid working. That kind of heat treatment includes baking finish and baking print. The term "amorphous crystals" referred to herein designates polymer crystals which are not oriented to a specific direction, and is generally called the "spherulite". For differentiating from the oriented crystals having planar orientation obtained by biaxial stretching, the term "amorphous crystals" is given herein.

Thus, the inventors of the present invention found that a laminated steel sheet having excellent post-heat-treatment workability is manufactured by the use of the half value width of shift peak obtained by Laser Raman spectrometry with the index

of degree of crystallinity of amorphous crystals (spherulite), and by the control of the half value width into a specific range.

There is a generally known relation between the volume fraction degree of crystallinity indicating the degree of formed crystalline polyester, (hereinafter referred to as the "degree of crystallinity"), and the density of resin laminating the metallic sheet, as given in eq. (1), ("Polymer solid structure, II" Kyoritsu Publication Co., Ltd. p305, (1974)).

$$\text{Volume fraction degree of crystallinity (\%)} = [(\rho - \rho_a) / (\rho_c - \rho_a)] \times 100 \quad (1)$$

where,  $\rho$  is the observed value of density, and  $\rho_c$  and  $\rho_a$  are the density of perfect crystal and perfect amorphous crystal, respectively.

Further study was given based on the above findings and the relation between the density and the degree of crystallinity of resin. The obtained result is shown in Fig. 1. Figure 1 gives the observed result of Raman spectra on PETs having different densities from each other, using a linear polarization light Ar<sup>+</sup> laser (514.5 nm of wavelength) as the laser light source. Since the half value width depends on, to some degree, the wave number resolution of the applied spectrometer, the wave number resolution of the spectrometer was set to 10.4 cm<sup>-1</sup> to assure the accuracy. As seen in Fig. 1, varied density of PET resin significantly varies the half value width of shift peak, (hereinafter referred to also as the "peak"), caused by the C=O stretch vibration in the vicinity of 1730 cm<sup>-1</sup> in the Raman spectra.

The shift peak caused by the C=O stretching vibration appears

at  $1730 \pm 20 \text{ cm}^{-1}$ , or in a range from  $1710$  to  $1750 \text{ cm}^{-1}$ , and is easily determined by one skilled in the art. Although the shift peak of PET caused by the  $\text{C}=\text{O}$  stretching vibration appears at  $1730 \text{ cm}^{-1}$ , it is observed in a range of  $1730 \pm 10.4 \text{ cm}^{-1}$  because the wave number resolution is  $10.4 \text{ cm}^{-1}$ . Generally the center of gravity of shift peak appears in the vicinity of  $1730 \text{ cm}^{-1}$ .

To this point, Raman spectra were observed on PETs of known densities to determine the relation between the density and the value width of shift peak. The result is given in Fig. 2. The figure shows that the density and the half value width of peak have a linear correlation.

The above result provides a correlation between the half value width of peak and the degree of crystallinity of resin laminating the steel sheet. Consequently, when a calibration curve for the half value width obtained from PET resins of known densities is prepared, the working curve can be used as an index of degree of crystallinity of amorphous crystal. In this manner, if the formation of amorphous crystals in the film by heat treatment is controlled so as the half value width of the peak to enter an appropriate range, there is appeared a possibility to prevent the deterioration of workability for film after heat treatment.

Then, the relation between the crack generation and the half value width used as the index of degree of crystallinity of amorphous crystal, (or the degree of crystallinity), was studied. There were prepared a laminated metallic sheet on which cracks appeared by DuPont impact working after the heat treatment at  $180^\circ\text{C}$  for 15 minutes, and a laminated metallic sheet which did

not generate cracks by DuPont impact working after the heat treatment at 180°C for 15 minutes. Additionally, a metallic sheet as-laminated state without subjecting to heat treatment was also prepared. Each of the metallic sheets was polished on a cross section. Laser light was radiated normal to the cross section of the resin layer, and the resulting Raman scattered lights were observed. A linear polarization light Ar<sup>+</sup> laser (514.5 nm of wavelength) was used as the laser light, and the incidence condition was that the polarization direction was in parallel to the thickness direction of the film cross section. The laser light was converged to about 1  $\mu\text{m}$  on the surface of sample using a lens ( $\times 100$  magnification). In the present invention, the observation was given under a condition that the polarization direction of the linear polarization light becomes parallel to the thickness direction of the film cross section because the condition is most suitable for the evaluation of amorphous crystals which have poor orientation. When the polarization direction is set to normal to the thickness direction of the film cross section, (i.e. parallel to the film surface), the degree of crystallinity of crystals having plane orientation by the stretch during film-forming stage can be evaluated. On the other hand, when the polarization direction is set to parallel to the thickness direction of the film cross section, the degree of crystallinity of amorphous crystals can be evaluated. While moving the incidence position at 1  $\mu\text{m}$  pitch in the thickness direction on the resin layer cross section, the Raman spectra were sequentially observed. From thus obtained data, the half value width of shift peak caused by the



C=O stretching vibration in the vicinity of  $1730\text{ cm}^{-1}$  was determined, and the values were plotted along the resin thickness from the interface between the metallic sheet and the resin to the resin surface, which plots are shown in Fig. 3 and Fig. 4. Figure 3 shows the observed values for the laminated metallic sheets which generated cracks in the film. Figure 4 shows the observed values for the laminated metallic sheets which did not generate cracks in the film.

Figures 3 and 4 show that the half value width of as-laminated metallic sheets without subjected to heat treatment gave almost constant values in the vicinity of  $25\text{ cm}^{-1}$  in the thickness direction. However, the half value width in the vicinity of surface of resin after heat treatment, (calculated as the average value among three observed values from the surface to  $3\text{ }\mu\text{m}$  in depth at an interval of  $1\text{ }\mu\text{m}$ ), gave  $21.2\text{ cm}^{-1}$  in Fig. 3, and  $22.9\text{ cm}^{-1}$  in Fig. 4. These show that the laminated metallic sheet which generated cracks gave high degree of crystallinity of amorphous crystals on the surface of resin after heat treatment, while the laminated metallic sheet which did not generate cracks gave low degree of crystallinity of amorphous crystals on the surface of resin after heat treatment.

Consequently, the increase in the degree of crystallinity of amorphous crystals resulting from the heat treatment becomes a cause of crack generation during the working stage after the heat treatment. In addition, it was found that the degree of crystallinity of amorphous crystals after the heat treatment depends on the half value width on the surface of film.

Next, the heat treatment condition was varied to investigate

the relation between the half value width of peak caused by the C=O stretching vibration on the film surface observed under the same condition as above, (calculated as an average of three points counted from surface), and the crack generation in the film caused by the DuPont impact working. The result revealed that, if only the half value width of the film surface layer after the heat treatment is  $22\text{ cm}^{-1}$  or larger, crack generation is suppressed, while the half width of the film surface layer after the heat treatment is smaller than  $22\text{ cm}^{-1}$ , cracks are generated. That is, independent of heat treatment conditions such as temperature condition and heat treatment time, if the half value width of the film surface layer after the heat treatment is  $22\text{ cm}^{-1}$  or larger, a laminated metallic sheet for can having excellent workability after the heat treatment is obtained.

In the present invention, the upper limit of half value width of peak is specified to  $25\text{ cm}^{-1}$  or smaller, since the half value width of PET resins in a perfect amorphous state is about  $25\text{ cm}^{-1}$ , the half value width of  $25\text{ cm}^{-1}$  is accepted as a state substantially free from crystals. Therefore, the range of half value width of peak on the film surface is specified to a range from the state that no amorphous crystal having  $25\text{ cm}^{-1}$  of half value width exists to the state of a degree of crystallinity of amorphous crystals specified by  $22\text{ cm}^{-1}$  of half value width.

As the polyester resin containing about 50% by mole or more of PET according to the present invention, resins containing polyethylene terephthalate as the main component can be widely used. Examples of those resins are polyethylene terephthalate

(homopolymer), poly(ethylene terephthalate-co-isophthalate) varying the concentration of isophthalic acid, and copolymers of terephthalic acid and/or isophthalic acid with a diol such as propylene glycol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, and cyclohexane dimethanol. These resins may be used separately or mixing them together. A single layer may be applicable, and multilayered resin composed of two layers or more of different ingredients may also be applicable. Even when copolymer resin, mixed resin and/or multilayered resin is used, the percentage of PET is about 50% by mole or more. According to the present invention, preferable percentage of PET is in a range from about 80 to 100% by mole, and more preferably from about 85 to about 90% by mole.

Applicable metallic sheet in the present invention includes various types of surface-treated steel sheets and light metal sheets of aluminum, copper, and their alloy. Applicable surface-treated steel sheet includes cold-rolled steel sheet which is treated by annealing and then by secondary cold-rolling, followed by one or more of surface treatment such as zinc-base plating, tin plating, nickel plating, chromium plating, tin and chromium two layer plating, electrolytic chromic acid treatment, chromic acid treatment, and phosphoric acid treatment. Widely applicable light metal sheet includes pure aluminum sheet, aluminum alloy sheet, and copper alloy sheet.

According to the present invention, the polyester resin may laminate at least one side of the metallic sheet. Current industrial applications often laminate on both sides of the

metallic sheet. Although the thickness (total thickness) of the polyester resin for laminating is not specifically limited, it is preferably in a range from 5 to 50  $\mu\text{m}$ . If the total thickness is 5  $\mu\text{m}$  or larger, the workability of lamination improves, and sufficient working corrosion resistance is attained. If the total thickness is not larger than 50  $\mu\text{m}$ , economical advantage is attained even compared with epoxy-base paints which are widely used in the can manufacturing field.

For improving beautiful appearance, coloring agent such as pigment and dye may be added to the resin film. For providing slidability, inorganic lubricating agent, antistatic agent, and the like may be added to the resin film. The method for thermocompression bonding coating of resin film on the surface of metallic sheet is not specifically limited. Generally a thermofusion type laminating unit shown in Fig. 5 is applied. The metal strip 2 heated in the heater 1 is clamped between a pair of lamination rolls 4. By applying a specified lamination roll pressing force to the strip 2, the resin film 3 continuously laminates on one side or both sides of the metal strip 2. In this case, it is applicable to form an adhesive layer between the film and the metallic sheet, thereby conducting lamination via the adhesive.

After the thermocompression bonding of resin film, quenching is preferably applied. Quenching prevents the formation of amorphous crystals in the film, which is advantageous in workability. To prevent the formation of amorphous crystals in the lamination stage, it is preferable to bring the film to a

glass transition point or lower temperature thereof within 5 seconds.

### **Examples**

Examples of the present invention are described in the following along with Comparative Examples. To various types of metallic sheets shown in Table 1, various types of polyester resins shown in Table 1 were laminated using the lamination unit shown in Fig. 5, and adjusting the lamination conditions (heating temperature of metal strip, lamination control temperature, cooling condition after thermocompression bonding of polyester resin film, and the like). Then, heat treatment was applied to the laminated metallic sheets under the condition given in Table 1 to prepare the respective samples.

Each of the samples after heat treatment was buffed on a cross section. Laser Raman spectrometry using a linear polarization laser light was applied to determine the Raman spectra of the resin layer under a condition that the polarization direction is vertical to the film plane, thus investigated the half value width of peak caused by the C=O stretching vibration in the vicinity of  $1730\text{ cm}^{-1}$  of Raman shift.

The observation of Raman spectra was done by a commercially available NRS-2000 Laser Raman spectrometer (JASCO International Co., Ltd.) The conditions of observation are described below.

The incident light was Ar<sup>+</sup> laser (514.5 nm of wavelength), and the laser light was converged to about 1  $\mu\text{m}$  on the sample surface using a lens (x100 magnification). The laser light

intensity was 2 mW on the sample surface. The slits were adjusted to 200  $\mu\text{m}$  for the slit 1, and to 400  $\mu\text{m}$  for the slit 3 and the slit 5. The wave number resolution was set to  $10.4\text{ cm}^{-1}$ . The observation time was 5 seconds x 2 per one observation point, with the aperture of 200  $\mu\text{m}$ . The observation was given at 1  $\mu\text{m}$  pitch in the thickness direction, and the average value of three points counted from the film surface was calculated, which average value was adopted as the half value width of the film surface layer. Since the laser light emitted from the laser oscillator is a linear polarization light having high purity, the observation did not apply polarizer.

The evaluation of workability after heat treatment was given as follows. The material was cut to 100 mm x 100 mm in size. The cut sample was placed in a hot air circulation furnace which was controlled to a specified temperature in advance. After a predetermined period, the sample was taken out from the furnace. Detail set temperature and treatment time in the furnace for Examples and Comparative Examples are shown in Table 1. After the heat treatment, the sample was subjected to DuPont impact test (1/4 inch of punch tip diameter, 1.0 kg of weight, and 300 mm of weight drop height) by facing the target laminate surface down. Only the resulted convex portion was immersed in a 0.5% saline solution, while applying 6.2 V to the electrode and the laminated metallic sheet in the saline solution, thus reading the leak current after 10 seconds. The sample giving less than 0.1 mA of leak current was judged to good one. The result is given in Table 1 and Fig. 6.

Table 1

	Film		Metallic sheet		Heating temp. of metallic sheet (°C)	Lamination roll temp. (°C)	Time until cooling (sec)	Heat treatment condition	Half value width of film surface layer after heat treatment (cm <sup>-1</sup> )	Leak current from worked portion (mA)
	Material <sup>*1</sup>	Thickness (μm)	Material	Thickness (μm)						
Example 1	A	20	TFS <sup>2</sup>	0.3	220	80	0.7	180°C x 5 min	23.6	less than 0.01
Example 2	A	20	TFS <sup>2</sup>	0.3	220	80	0.7	180°C x 15 min	23.2	less than 0.01
Example 3	A	20	TFS <sup>2</sup>	0.3	220	80	0.7	180°C x 30 min	22.9	less than 0.01
Example 4	A	20	TFS <sup>2</sup>	0.3	210	80	0.7	180°C x 15 min	24.2	less than 0.01
Example 5	A	20	TFS <sup>2</sup>	0.3	215	80	0.7	180°C x 15 min	23.8	less than 0.01
Example 6	A	20	TFS <sup>2</sup>	0.3	222	80	0.7	180°C x 15 min	22.8	0.03
Example 7	A	20	TFS <sup>2</sup>	0.3	223	80	0.7	180°C x 15 min	22.1	0.08
Example 8	A	20	TFS <sup>2</sup>	0.3	220	80	0.7	150°C x 15 min	23.5	less than 0.01
Example 9	A	20	TFS <sup>2</sup>	0.3	220	80	0.7	220°C x 15 min	22.9	0.02
Example 10	A	20	TFS <sup>2</sup>	0.3	215	80	0.7	130°C x after 15 min 180°C x 15 min	23.4	0.03
Example 11	A	12	TFS <sup>2</sup>	0.2	223	110	1.2	180°C x 15 min	22.9	0.06
Example 12	A	50	TFS <sup>2</sup>	0.2	223	110	1.2	180°C x 15 min	24.1	less than 0.01
Example 13	A	5	TFS <sup>2</sup>	0.15	210	110	1.2	180°C x 15 min	23.5	0.05
Example 14	A	20	Thin plating tin plate	0.3	220	80	0.7	180°C x 15 min	23.2	less than 0.01
Example 15	A	20	Aluminum alloy	0.3	220	80	0.7	180°C x 15 min	23.4	less than 0.01
Example 16	B	20	TFS	0.3	220	80	3.6	180°C x 15 min	23.1	less than 0.01
Example 17	C	20	TFS	0.25	250	100	0.7	130°C x 15 min	22.5	0.02
Example 18	C	20	TFS	0.25	245	100	0.7	130°C x 15 min	23.2	0.01
Example 19	C	20	TFS	0.25	252	100	0.7	130°C x 15 min	22.3	0.03
Comparative example 1	A	20	TFS	0.3	225	80	0.7	180°C x 2 min	21.6	4.6
Comparative example 2	A	20	TFS	0.3	225	80	0.7	180°C x 5 min	21.4	15
Comparative example 3	A	20	TFS	0.3	225	80	0.7	180°C x 10 min	21.0	20
Comparative example 4	A	20	TFS	0.3	225	80	0.7	180°C x 15 min	20.8	32
Comparative example 5	A	20	TFS	0.3	225	80	0.7	180°C x 30 min	20.5	38
Comparative example 6	A	20	TFS	0.3	222	80	0.7	180°C x 30 min	21.8	0.2
Comparative example 7	C	20	TFS	0.25	255	100	0.7	130°C x 15 min	21.7	2.2
Comparative example 8	C	20	TFS	0.25	260	100	0.7	130°C x 15 min	20.5	18
Comparative example 9	C	20	TFS	0.25	252	100	0.7	180°C x 5 min	21.9	0.9
Comparative example 10	C	20	TFS	0.25	252	100	0.7	130°C x after 15 min 180°C x 15 min	21.4	3.2

\*1 Film A: isophthalic acid copolymerized PET (12% by mole of isophthalic acid copolymerization percentage)

Film B: isophthalic acid copolymerized PET (8% by mole of isophthalic acid copolymerization percentage)

Film C: homo-PET

\*2 TFS: tin-free steel

Table 1 and Fig. 6 show that the behavior of leak current at worked portion significantly varies at the half value width of  $22\text{ cm}^{-1}$  on the film surface. Smaller than  $22\text{ cm}^{-1}$  of half value width on the film surface, corresponding to Comparative Examples, suddenly increased the leak current at the worked portion, and deteriorated the workability. Inversely, at or larger than  $22\text{ cm}^{-1}$  of half value width on the film surface, corresponding to Examples of the present invention, gave small leak current, and showed good workability.

#### **INDUSTRIAL APPLICABILITY**

Therefore, according to the present invention, a laminated metallic sheet for can having excellent workability after heat treatment is obtained. Since a metallic sheet laminated by a polyester-based resin containing polyethylene terephthalate as the main component, according to the present invention, has excellent workability after heat treatment, the metallic sheet is suitable for the material of metallic can and can lid which are formed by working after the heat treatment such as baking finish and baking print.